Trifluoromethyl Hypochlorite

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FLUOROXY-PERFLUOROALKYL compounds, R_FOF, are now well known[1] and alkyl hypochlorites have been known for decades; however, no perfluoroalkyl hypochlorites have previously been prepared. We report the synthesis and characterization of trifluoromethyl hypochlorite, CF_3OCl. The new compound, b.p. $-47°$, m.p. $-164°$, was identified by chemical analysis, molecular weight (Found: 120·7), and ^{19}F n.m.r. spectroscopy. The ^{19}F n.m.r. spectrum (56·4 MHz.) of liquid CF_3OCl at $-78°$ consists of a singlet at $\delta + 71·9$ (CCl_3F as external standard), indicating that the fluorine atoms are equivalent and bonded to carbon.

The i.r. spectrum of the gas (Monel cell, AgCl windows) consists of bands at 1262s, 1220s, (shoulder), and 1205s (C–F region), 925mw, and 665mw cm.$^{-1}$. The band at 665 cm.$^{-1}$ may be associated with the O–Cl stretching frequency as the alkyl hypochlorites have bands in this general region which have been associated with the stretching of this bond.[2]

Trifluoromethyl hypochlorite can be prepared in nearly quantitative yield from the reaction of carbonyl fluoride and chlorine monofluoride in the presence of caesium fluoride catalyst at $-20°$. Fractionation (nickel/Kel-F vacuum system) of the reaction products through traps at $-140°$ and $-196°$ yields pure CF_3OCl which is retained as a pale yellow liquid in the $-140°$ trap.

We have also prepared and characterized several other hypochlorites by the method described. For example, heptafluoroisopropyl hypochlorite, iso-C_3F_7OCl, results from the caesium fluoride-catalyzed reaction between hexafluoroacetone and chlorine monofluoride at $-20°$. In an analogous reaction, the inorganic hypochlorite, SF_5OCl, has been prepared by chlorofluorination of thionyl tetrafluoride at $-20°$ in the presence of caesium fluoride. The identity of both compounds was confirmed by elemental analysis.

Trifluoromethyl hypochlorite has excellent thermal stability and can be heated at 100° in a stainless-steel cylinder for several days with no apparent decomposition. The other hypochlorites we have prepared appear to be somewhat less stable (or more reactive) than CF_3OCl. All the perfluoroalkyl hypochlorites, however, appear to be much more stable than their alkyl counterparts, many of which are very difficult to isolate.[3]

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